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Trace Impurity Removal from Air

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Abstract. In addition to Nitrogen, Oxygen and Argon, ambient air contains many trace impurities. These impurities include moisture, Carbon Dioxide, Oxides of Nitrogen and light Hydrocarbons. Prior to cryogenic distillation of air to produce Nitrogen, Oxygen and Argon these trace impurities have to be removed since, some of these constitute a safety hazard in the cryogenic plant. A significant amount of information is available in the literature for the removal of Water and Carbon Dioxide from air. However, only limited information is available for the removal of other trace impurities. We discuss the results of an experimental study on the removal of these trace impurities from air.

These days, air pre purification is carried out primarily by adsorption based technologies. There are two main choices: Thermal Swing Adsorption (TSA) processes, and Pressure Swing Adsorption (PSA) processes. Main differences between these two approaches and the trace impurity removal results are discussed.

Keywords: adsorption, trace removal, nitrous oxide, pre-purification units, PPU, air separation, ASUs

Introduction

In addition to Nitrogen,Oxygen and Argon, ambient air contains many trace impurities. These impurities include moisture, Carbon Dioxide, Oxides of Nitrogen, light Hydrocarbons and others. For cryogenic air separation plants, these impurities may be classified into four main categories: plugging compounds, flammable compounds, reactive compounds and corrosive compounds. A typical list is (IGC Document Doc 65/99/EFD):

1. Plugging components: H_2O, CO_2, C_2H_2 and N_2O
2. Flammable or reactive components: CH_4, C_2H_6, C_3H_8, C_2H_2, C_2H_4, C_3H_6, C_{4^+}, NO_x and O_3
3. Corrosive components: SO_2, SO_3, H_2S, Cl_2, HCl, NH_3, Other Sulfur Compounds and Chlorides

Typical levels of these impurities in air are listed in Table 1.

Air separation plants produce Nitrogen, Oxygen, Argon and other air gases by cryogenic distillation. A typical arrangement for an air separation plant is shown in Fig. 1. Ambient air is compressed to high pressure and enters the cooling system. Some of the trace impurities, mainly corrosive compounds are removed in the cooling system. The cooler air then enters the pre-purification unit (PPU). The remaining corrosive compounds, Moisture, Carbon Dioxide, Acetylene and portions of the remaining trace impurities are removed in the PPU units. The clean air then enters the main heat exchanger. It is further cooled to cryogenic temperatures by exchanging against the cold product stream produced by the distillation column. Cryogenic vapor mixture now enters the high-pressure distillation column. Oxygen rich liquid from the high-pressure column is fed to the low-pressure distillation column. Pure Oxygen is produced in this column. Liquid Oxygen (LOX) collects in the bottom of this column as liquid sump around the thermosyphon re-boiler. The primary concern with the trace impurities entering the distillation system with feed air is their concentration in the LOX sump. Air separation units (ASUs) are designed

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Table 1. Typical levels of trace impurities in air.

Component		PPMv
Water		Saturated
Carbon dioxide	CO_2	400
Nitrous oxide	N_2O	0.35
Methane	CH_4	2–25
Ethane	C_2H_6	0–5
Propane	C_3H_8	0–2
Acetylene	C_2H_2	0–1
Ethylene	C_2H_4	0–3
Propylene	C_3H_6	0–1
$C_4{}^+$ HCs		0–1
NO_x	$NO + NO_2$	0–1
Sulfur dioxide	SO_2	0–0.2
Sulfur trioxide	SO_3	0–0.002
Hydrogen sulfide	H_2S	0–0.2
Ammonia	NH_3	0.05–0.13
Hydrochloric acid	HCl	0.01–0.07
Chlorine	Cl_2	0.002–0.03
Ozone	O_3	0–0.2

Table 2. Allowable trace impurities from PPU system. $P = 1.2$ bara, Liquid purge = 0.5%.

		PPMv
Nitrous oxide	N_2O	0.09
Methane	CH_4	Not a concern
Ethane	C_2H_6	0.25
Propane	C_3H_8	0.1
Acetylene	C_2H_2	0.0005
Ethylene	C_2H_4	0.2
Propylene	C_3H_6	0.035
C_{4+} HCs		0.005

such that the concentrations of the trace impurities meet most restrictive of the following criterions:

- 1/2 the Solubility limit for plugging compounds in LOX, or
- Maximum of 1% of flammability limit for flammable compounds, or
- 500 vpm total hydrocarbons in LOX on CH_4—equivalent basis.

The most common practice to maintain these levels of trace impurities in the LOX sump is to take a LOX purge from the sump. The LOX purge requirement depends upon the operating pressure of the sump. Table 2 lists the allowable levels of trace impurities from the PPU units at a typical (0.5%) LOX purge at a sump pressure of 1.2 bara to meet the above mentioned trace impurity requirements in the LP (Low Pressure) column LOX sump. The % LOX purge is defined as:

LOX taken as purge/Total Oxygen Product
((Gaseous Oxygen) GOX + LOX)

The allowable levels go up in direct proportion to the LOX purge. Therefore, a higher LOX purge is required

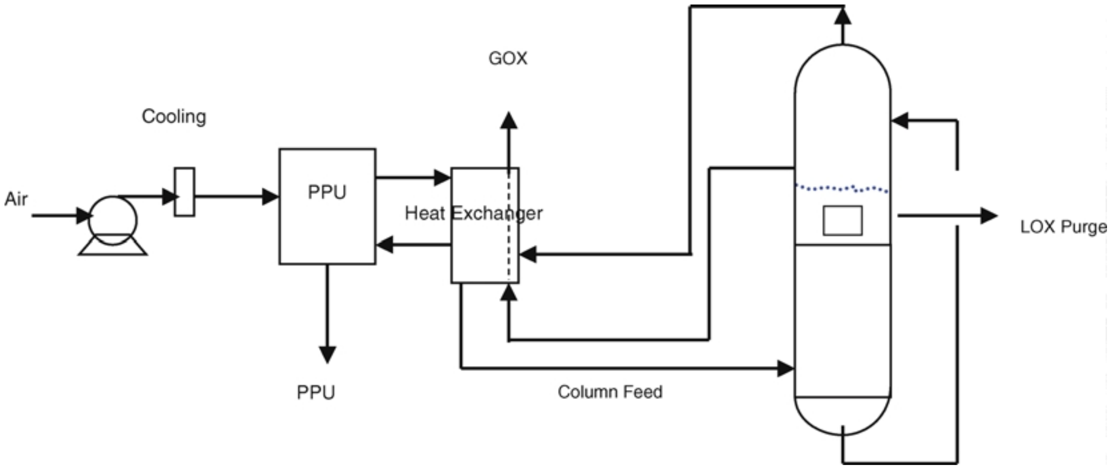

Figure 1. Typical air separation plant.

if the level of impurities exiting the PPU is higher. Generally the higher LOX purge is an acceptable solution but it adds to the cost of the plant. Another possible solution is to remove these impurities in the PPU units.

Pre-Purification Units

These days, air pre purification is carried out primarily by adsorption based technologies. There are two main choices:

1. Thermal Swing Adsorption (TSA) processes, and
2. Pressure Swing Adsorption (PSA) processes.

PSA is more recent technology than TSA (Kumar, 1987). However it is being accepted as the method of choice for many air pre purification plants. The primary differences between these two processes are:

1. The adsorbents used for purification are different in the two processes. Equilibrium isotherms for the adsorbents used in TSA PPUs are more non-linear than for the adsorbents used in PSA PPUs.
2. TSA processes require thermal energy to regenerate the adsorbent. PSA requires compression energy. Therefore, TSA may be a preferred option if a cheap source of energy is available. However, if this is not the case, the total energy cost for a PSA PPU is lower than for a TSA PPU.
3. PSA processes operate on a much shorter cycle than the TSAs (several minutes vs. several hours). The reason for this behavior is that the effective working capacity for the PSA PPUs is lower than for TSA PPUs (almost a ratio of 10:1). This results in larger bed volumes for PSA PPUs than for TSA PPUs for the same cycle time. Therefore, to keep the vessel sizes reasonable, the cycle times for PSA PPUs are reduced. This results in choosing a TSA PPU for very large air separation plants.
4. PSA requires much larger quantities of purge gas than TSA (~40% vs. ~10% of feed air). Therefore, a TSA process is preferred if available purge gas quantity is in short supply. This may be the case when the plant produces multiple products at high recoveries.

Overall, in instances where applicable, the capital and operating costs of PSA PPUs are usually lower than TSA PPUs.

Another difference between TSA and PSA is that for TSA PPUs, both average and the peak concentrations of the impurity in the PPU effluent need to be considered for design, since, these two values are quite different, but for PSA PPUs these two values are quite similar therefore, only one concentration value needs to be considered. Typical trace impurity breakthrough curves for these two systems are compared in Fig. 2 on a dimensionless basis. It should be noted that the impurity scales on the Y-axis for the two processes are different. These differences result in designing the TSA

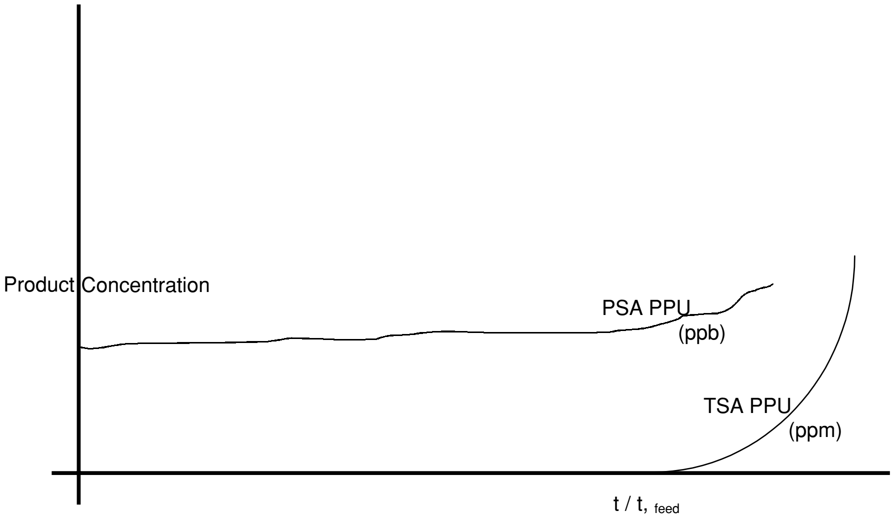

Figure 2. Typical breakthrough curves from PSA and TSA PPUs.

and PSA PPUs for different level of impurity in the clean air produced by the PPU and fed to the cryogenic distillation column.

TSA-PPU Process

The thermal-swing pre-purification process has been in use for past several decades (Reyhing and Solin, 1983). The five main steps involved in the process are:

1. *Feed/Adsorption.* A typical TSA-PPU adsorber uses a dual layer design, with an activated alumina layer to remove H_2O, followed by a zeolite layer to remove the other components. NaX type zeolite is generally used in the second layer. The exact split between these two layers depends upon the operating conditions of the unit. The adsorption step is terminated when the effluent concentration of a key component, most likely CO_2, has reached a predetermined value (0.1 to 1 ppm). Typical duration of this step is 4 h. However, systems with as short as 2 h of feed duration have been designed and built.
2. *Blowdown.* Following breakthrough of the key component, the adsorber is slowly vented until atmospheric pressure is reached in the vessel. Duration of this step is in the order of 10 min.
3. *Regeneration—Heating.* The main source of energy in TSA-PPU processes is the thermal pulse administered to the adsorber during this step. Following blowdown, countercurrent to feed flow, dry CO_2free clean air is passed through the adsorber. The regeneration stream is heated to a desired temperature such that the impurities adsorbed during the feed step are removed due to lower adsorption capacity. A commonly used regeneration temperature is 300°F. However, lower regeneration temperatures have also been used. Required regeneration gas quantity goes up as the regeneration temperature goes down (Kumar and Dissinger, 1985). Therefore, process optimization is required to design this step.
4. *Regeneration—Cooling.* Following the heating step, the adsorbent is cooled by continuing to flow the regeneration stream through the vessel in the same direction as above. The regeneration stream is not heated during this step. The heat stored in the bed during the previous step exists the vessel during this step. At the end of this step the bed temperature is close to the feed temperature.

   The duration of regeneration steps (heating and cooling) for a two bed system is given by:

$$\begin{aligned}&\text{Regeneration step duration}\\&\quad = \text{Feed step duration} - \text{Blowdown step}\\&\qquad \text{duration} - \text{Re-pressurization step duration.}\end{aligned}$$

   To maintain proper heating and cooling of the vessel, the ratio of the cooling to heating step duration is generally between 1.3 to 1.7 (Kumar et al., 2000).
5. *Re-pressurization.* The adsorber vessel is repressurized to the operating pressure of the feed step, using either feed air or the clean air generated by the on-line bed. The choice of stream used for re-pressurization depends upon many considerations previously published (Kumar et al., 2000). Duration of this step is in the order of 15 min.

TSA-PPU Trace Impurity Removal Experiments

Figure 3 illustrates the experimental setup. The selected hazardous trace impurities (N_2O, C_2H_2, C_2H_4, C_2H_6, C_3H_6, C_3H_8 and n-C_4H_{10}) were injected into the dehydrated, CO_2—free air stream. The concentration ratios of these components were determined based on plant operating experience. Gas samples were taken from the system at three points:

(1) Immediately after the gas injection point,
(2) At a certain height within the packed bed, and
(3) At the PPU effluent end.

In the experimental set up, the bed was packed in a 6 ft long × 1.93 inch diameter vessel. The column was packed with the CO_2 removal adsorbent (NaX) and regenerated at 300°F after each experiment. The experiments were carrier out at 100 psig and 70°F feed pressure and temperature, respectively. Gas sample analysis was performed using a Nicolet® Magna™ 550 Fourier Transfer Infrared Spectrometer (FT-IR) which used a CIC Photonics fixed multi-pass corrosion resistant gas cell. The FT-IR was specifically calibrated for this work using a synthetic spectrum method and various high purity gases representing the hazardous trace impurity mixture.

In each experiment, the adsorber was placed on-stream until the designated key component (N_2O) had broken through completely and had reached its feed concentration.

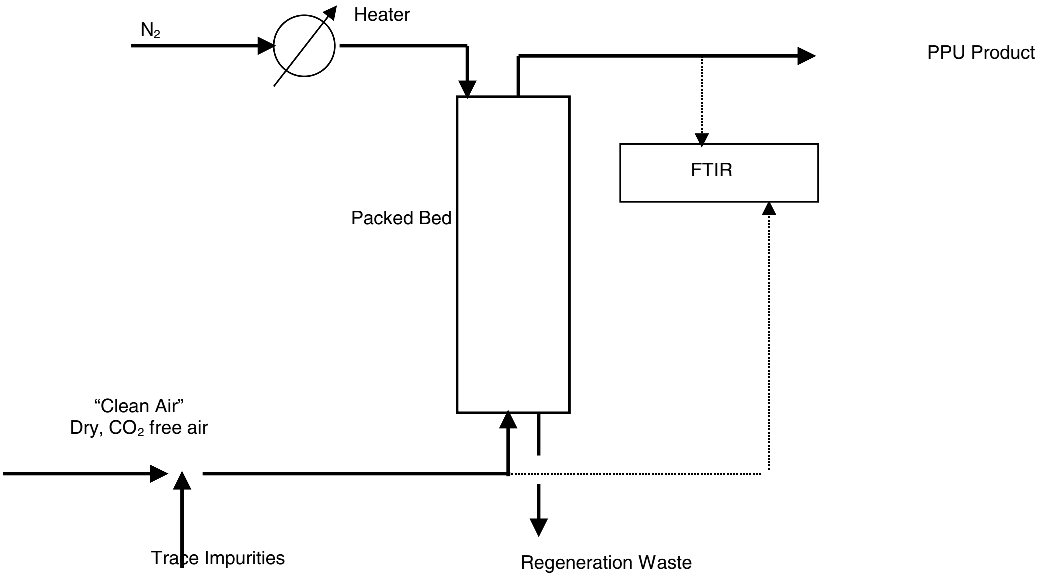

Figure 3. Flow diagram of TSA-PPU trace removal experimental set up.

TSA-PPU Results and Discussion

The performance of the existing TSA-PPU adsorbent (NaX) is given in Table 3. The % amount removed is calculated directly from the component mass balance as the ratio of the total mass of that component removed in a given cycle to the total mass of that component fed to the bed during the cycle:

$$\text{Removal} = \left(\int_0^{t,\text{co}_2} Y_{\text{in}} - \int_0^{t,\text{co}_2} Y_{\text{out}}\right) \Big/ \int_0^{t,\text{co}_2} Y_{\text{in}}$$

From Table 3 we see that at CO_2 breakthrough (0.1 ppm) 40% removal of N_2O, Ethylene, and Propane is achieved. Only 10% Ethane removal is achieved. The other compounds are 100% removed as these breakthrough only after CO_2 breakthrough.

To facilitate the removal of these trace impurities in TSA PPUs, a new adsorbent was developed. However, instead of the typical two layers a bed with three layers was used:

Table 3. Trace removal by existing adsorbents in TSA PPU. % Removal at 0.1 ppm CO_2 breakthrough.

		Feed (ppm)	Peak (ppm)	% Removal
Nitrous oxide	N_2O	0.35	0.45	40
Ethane	C_2H_6	1.4	1.5	10
Propane	C_3H_8	1.6	1.7	40
Ethylene	C_2H_4	1.5	2.5	40
Propylene, butane, water and acetylene				100

1. First layer, at the feed end to remove water,
2. Second layer to remove Carbondioxide and the hydrocarbons as mentioned above, and
3. The third top layer to remove N_2O and the remaining trace hydrocarbons not removed in the first two layers. A proprietary adsorbent is used as the third layer (Kumar et al., 2002). It is a composite zeolitic adsorbent made by mixing CaA and CaX type zeolites.

Typical layer arrangement is shown in Fig. 4. The first layer in Fig. 4 may consist of a single layer to remove moisture and other trace impurities or of two separate layers, the first of which removes moisture and the second removes CO_2 and other trace impurities. The experiments described in the previous section were repeated under the same conditions for this new adsorbent and the results are shown in Table 4. The new adsorbent succeeds in completely removing N_2O and ethylene and there is more than twofold increase in the retention of other saturated hydrocarbons.

PSA PPU Process

Pressure Swing Adsorption Pre-Purification Unit (PSA PPU) was developed and employed for air purification

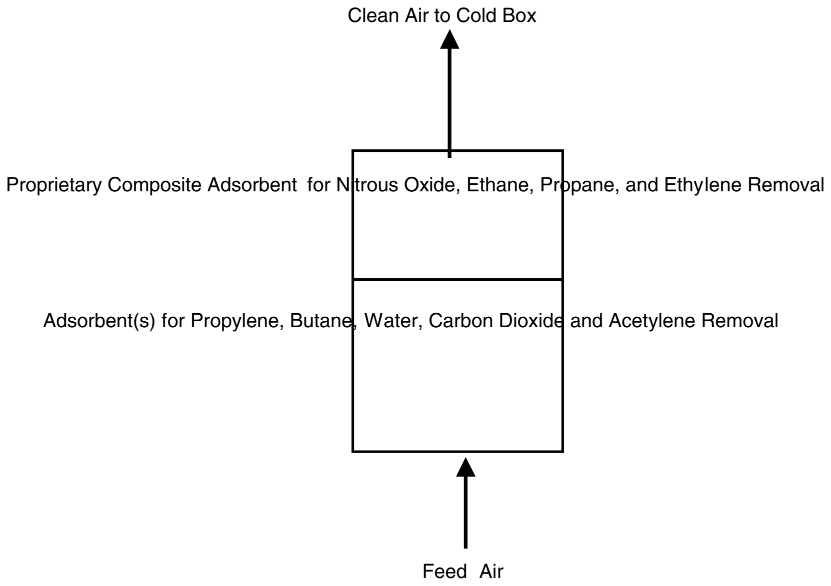

Figure 4. TSA PPU trace removal approach.

in the late 1980s (Kumar, 1987). Typical PSA PPU process consists of four main steps:

1. *Feed/Adsorption*. Hazardous trace impurities including H_2O, CO_2 and others are removed from the ambient air by adsorption on a selective adsorbent, generating a purified air stream which is fed to the cryogenic air separation plant. Activated alumina (Jain, 1993) based adsorbents are typically used in PSA PPU because of their relatively high working capacity for both CO_2 and H_2O removal under PSA mode. The adsorption step typically lasts about 5–30 min, and is usually operated at close to ambient temperature. The feed pressure varies from 3 to 10 atm.
2. *Blowdown*. When the CO_2 concentration in the purified air streams reaches a predetermined level (ppb), the adsorption step is terminated, and the pressurized gases in the adsorber are vented to atmosphere for a short period of time (about 1–2 min). The pressure and temperature in the vessel after venting are close to ambient conditions.

Table 4. Trace removal performance of new TSA PPU adsorbent. % Removal at 0.1 ppm CO_2 breakthrough.

		Feed (ppm)	% Removal
Nitrous oxide	N_2O	0.35	100
Ethane	C_2H_6	1.4	85
Propane	C_3H_8	1.6	98
Ethylene	C_2H_4	1.5	100

3. *Purge*. Although some adsorbed gases are desorbed during the venting step, the adsorbent needs further regeneration to recover its working capacity. Normally a low pressure CO_2 free dry gas stream generated as waste from the cryogenic distillation column is used to purge the PPU vessel to regenerate the adsorbent at close to ambient temperature. The purge step time is usually shorter than adsorption step time.
4. *Re-pressurization*. After the purge step, the regenerated bed is re-pressurized with purified air stream prior to going onto the next adsorption step. Since a portion of the purified air stream from the other PPU bed is used for re-pressurization, effluent flow rate from the PSA PPU fluctuates during this time for a 2-Bed system. This results in flow rate fluctuations to the cryogenic distillation column. In cases where this is not desirable, a 3-Bed system is used to eliminate these flow rate fluctuations generated during the re-pressurization step (Kumar, 1996).

In the 1980s, PSA PPUs were first used on ASUs producing ~50 MTPD of Oxygen. However, recently PSA PPUs have been extended to larger size ASUs.

Multiple vessels (>3) are used to extend the range of PSA PPUs to 600 MTPD Oxygen plants.

PSA PPU Trace Removal Experiments

The flow diagram of PSA PPU trace removal experimental set up is shown in Fig. 5. Trace components including N_2O, C_2H_2, C_2H_4, C_2H_6, C_3H_6, C_3H_8 and n-C_4H_{10} were injected into ambient air and fed into the PSA PPU vessel which was packed with an activated alumina based adsorbent. In the experimental set up, the bed was packed in a 7 ft long × 5 inch diameter vessel. Volumetric purge to feed ratio of ~2 was used. The experiments were carrier out at 100 psig and 70°F feed pressure and temperature, respectively. Trace concentrations of different gas streams including feed, product, and samples from different bed locations were measured during the feed step. CO_2 was monitored with Horiba CO_2 analyzers and moisture was measured by Panametrics Hygrometers. The instrument used for N_2O and hydrocarbons detection in this work was a Nicolet® Magna™ 550 Fourier Transfer Infrared Spectrometer (FT-IR) which used a CIC Photonics fixed multi-pass corrosion resistant gas cell. The FT-IR was specifically calibrated for this work using different high purity gases. A computer software (OMNIC E.S.P. 5.0) which came with the FT-IR was used for data processing.

Cyclic experiments were carried out using the PSA cycles as described above. Cyclic steady state was examined by measuring transient concentration profiles of a selected trace component along the adsorbent vessel during the feed (adsorption) step. The performance of the adsorbent for trace removal was determined by the percentage removal of each trace component after cyclic steady state had established. The effluent concentration of each component as a function of time was recorded. The average concentration in the effluent during the feed step was used to calculate the removal efficiency.

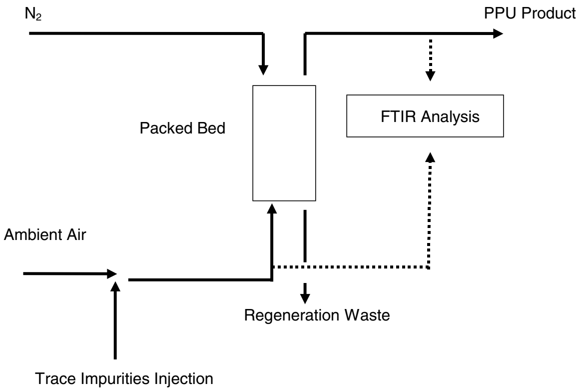

Figure 5. Flow diagram of PSA PPU trace removal experimental set up.

PSA PPU Results and Discussion

Table 5 lists the performance of the existing adsorbent for trace removal. This was measured after cyclic steady state had established. The percentage removal is calculated as:

$$\% \text{ Removal} = (\text{feed conc.} - \text{average effluent conc.})/\text{feed conc.} \times 100\%$$

The average effluent concentration was calculated from the trace concentration in the PPU product during the feed step. As shown in Table 5, the existing activated alumina adsorbent (Jain, 1993) can completely remove H_2O, CO_2 and C_2H_2 from air under normal PSA PPU operating conditions, but it can only remove about 40% of N_2O and hardly remove other non-C_2H_2 hydrocarbons. The partially or not removed trace components show a breakthrough type behavior. The peak value of the trace components sometimes exceed the feed concentration during the feed step due to the roll-up effect.

As shown above N_2O and C_2–C_4 hydrocarbons except C_2H_2 are not effectively removed by the existing PSA PPU adsorbent. To facilitate the removal of these trace impurities in PSA PPUs, a new adsorbent was developed (Deng et al., 2002). This is also a multi-composite adsorbent made by mixing activated alumina with CaA and NaX type zeolites. It is different than the one used in TSA PPU for trace removal.

Table 5. Trace removal by existing adsorbents in PSA PPU. % Removal at cyclic steady state.

		Feed (ppm)	% Removal
Nitrous oxide	N_2O	0.35	40
Ethane	C_2H_6	1.4	0
Propane	C_3H_8	1.9	5
Ethylene	C_2H_4	2	25
Propylene	C_3H_6	0.6	0
Butane	C_4H_{10}	1	0
Water and acetylene			100

Table 6. Trace removal performance of the new PSA PPU adsorbent. % Removal at cyclic steady state.

		Feed (ppm)	% Removal
Nitrous oxide	N_2O	0.35	100
Ethane	C_2H_6	1.4	40
Propane	C_3H_8	1.9	100
Ethylene	C_2H_4	2	98
Propylene	C_3H_6	0.6	97
Butane	C_4H_{10}	1	100
Water and acetylene			100

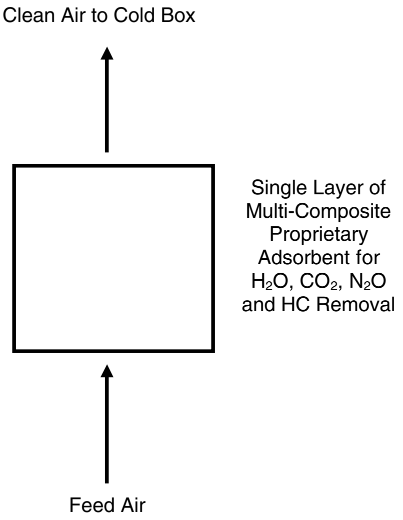

Figure 6. PSA PPU trace removal approach.

Similar cyclic experiments using the PSA PPU trace removal adsorbent were carried out in the same experimental set up as shown in Fig. 5 at similar operating conditions. In contrast to TSA PPU application, the entire bed was packed with the same adsorbent (Fig. 6). Table 6 lists the performance of the new adsorbent. The new adsorbent can effectively remove N_2O, C_2–C_4 hydrocarbons except C_2H_6, in addition to complete removal of H_2O and CO_2.

Conclusions

In addition to moisture and CO_2, N_2O has emerged as another trace contaminant which could be a safety hazard in air separation plants. Several methods are available to operate the plants safely including the traditional method of LOX purge. Another approach is suggested in which the trace impurities are removed in the Pre-Purification units used for Moisture and Carbondioxide removal:

1. Thermal Swing Pre-Purification units are able to remove N_2O and other Hydrocarbon trace contaminants using an additional layer of specifically designed composite adsorbent (Kumar et al., 2002).
2. Pressure Swing Pre-Purification units are able to remove N_2O and other Hydrocarbon trace contaminants along with moisture and CO_2 by using an entire bed of a different (than TSA) specifically designed multi-composite adsorbent (Deng et al., 2002).

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